# Glass Transition Temperature of Graphene/PMMA Nanocomposites

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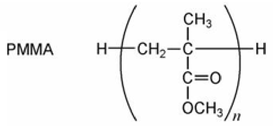
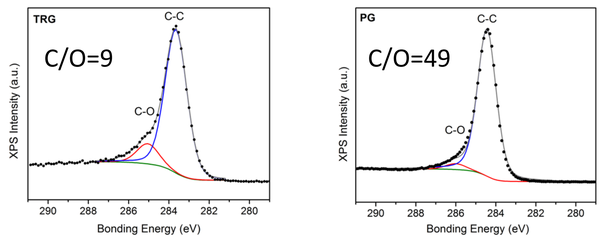
## Background:

Polymer nanocomposites are polymers with nanofillers dispersed in the polymer matrix. The use of graphene, which has outstanding electrical and mechanical properties, as the nanofiller can improve these characteristics of the host polymer. Previous studies on graphene polymer nanocomposites have reported that the incorporation of graphene may also raise the glass transition temperature (Tg), the temperature at which the polymer changes from a hard and brittle state to a rubber-like state. However, many other studies have also concluded that graphene has no effect. These scattered results have left the effect of graphene on the Tg unanswered. This research investigated the effect using two types of graphene and polymer of different stereo-regularity.

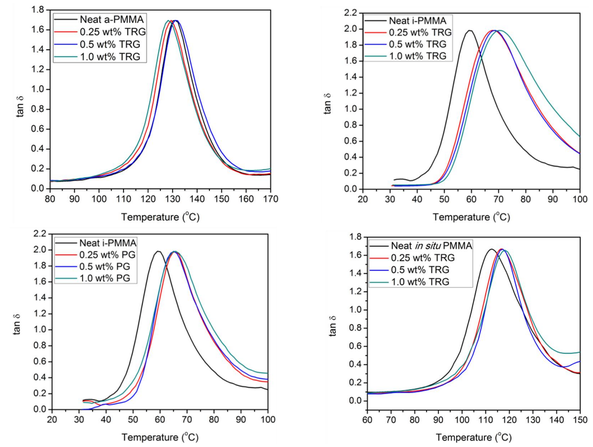
## Materials:



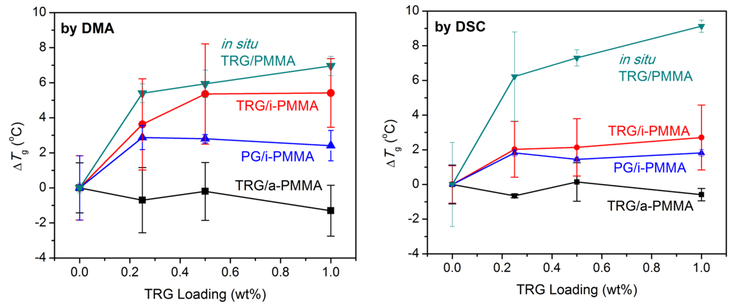




PMMA, poly(methylmethacrylate), was used as the polymer matrix with two kinds of graphene, TRG (thermally reduced graphene) and PG (near pristine graphene). Four nanocomposite systems were tested: solvent blended TRG/a-PMMA, TRG/i-PMMA, PG/i-PMMA, and *in situ* polymerized TRG/PMMA. Samples were made by dissolving in THF, precipitating in methanol, and drying in a vacuum oven. AIBN was used as the initiator for *in situ* polymerization. Samples were tested for Tg with Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC).

## Results:

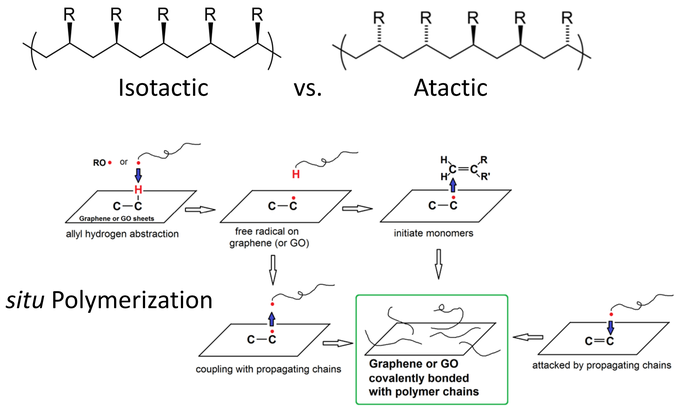



The DMA results (tan δ) are shown here. The Tg values for neat a-PMMA (124.6 °C) and i-PMMA (55.7 °C) agree with literature.[1] The neat *in situ* polymerized PMMA (110.9 °C) also agrees with literature for similar free radical polymerization at 65 °C.[2] A clear shift in the Tg is present for the TRG/i-PMMA, PG/i-PMMA and *in situ* TRG/PMMA nanocomposites.




A summary of the Tg change, ΔTg, from both DMA and DSC is shown above. Significant Tg changes were observed in TRG/i-PMMA, PG/i-PMMA, and *in situ* TRG/PMMA nanocomposites, while the TRG/a-PMMA nanocomposite showed no significant Tg change. The largest Tg increase was observed with the *in situ* TRG/PMMA nanocomposite.

## Discussion:




The Tg increase of the solvent blended graphene/i-PMMA nanocomposites can be attributed to the immobilization matrix of i-PMMA molecules. The alignment of the ester groups creates a higher interaction density between i-PMMA and graphene than a-PMMA. This allows for stronger interactions between the graphene and i-PMMA to create a shift in the Tg. The *in situ* polymerized nanocomposites showed the greatest Tg increase because some of the matrix PMMA is covalently bonded to the TRG.

## Conclusion:

In addition to improving electrical and mechanical properties, incorporation of graphene can also increase the Tg. Here we show that the effect of graphene on the Tg is dependent on the stereo-regularity of the host polymer and the processing method. These results show that an increase in Tg is obtainable by solvent blending graphene with i-PMMA as well as *in situ* polymerization of PMMA in the presence of graphene. Significant Tg increases were observed at low loadings of graphene. Therefore, higher glass transition temperatures can be achieved with graphene/polymer nanocomposites. Materials can then be used at higher temperatures without changing states.

Acknowledgements:
Ken-Hsuan Liao (UMN CEMS, DuPont)

Selected References:

1)T. Wallin, "Mechanical Properties of POlymer Nanocomposites Based on Functionalized Graphene Sheets," College of William and Mary, Virginia, 2010.
2) J. Wang, H. Hu, X. Wang, C. Xu, M. Zhang, and X. Shang, "Preparation and mechanical and electrical properties of graphene nanosheets-poly(methyl methacrylate) nanocomposites via in situ suspension polymerization," *Journal of Applied Polymer Science*, vol. 122, no. 3, pp. 1866–1871, Nov. 2011.